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Estimation of particle size using the Debye equation and the Scherrer formula for polyphasic TiO₂ powder

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Abstract. There are two methods to estimate the particle size from X-ray diffraction data: the Debye equation and the Scherrer formula. The main goal of this study is to describe the methodology of particle size estimation on the base of two these methods and to apply it to TiO₂ powder to determine the diameters and the mass content of anatase and brookite components. The studied nano-dispersed TiO₂ powder was synthesized by the sol-gel method. The proposed method of particle size estimation consists of several steps: 1. Approximation of diffraction peaks by Gaussians and calculation of initial values of particle size with the use of the Scherrer formula; 2. Iterations with the use of the Debye equation to obtain more accurate particle size values; 3. Calculation of the mass content of different components corresponding to the minimum R-factor.

1. Introduction

Titanium dioxide TiO₂ is an extensively applied compound due to high photosensitivity, non-toxicity, easy availability, pH and long-thermal and chemical stabilities, low cost [1]. In recent decade, advanced TiO₂-based photocatalysts have been promisingly suggested as the materials for removal of organic contaminants and disinfection of freshwater from algae [2], hygiene coatings to control and reduce populations of pathogenic bacteria [3], CO₂ photoreduction in the presence of water vapor to produce solar fuels (CO and CH₄) [4]. In the field of alternative energetics, TiO₂ is used as a matrix of photoactive layer in dye-sensitized solar cells [5]. There are three phases of titanium dioxide: rutile, anatase, and brookite. Photocatalytic activity can be enhanced through mixing of several phases of TiO₂: for an example, anatase/rutile, brookite/rutile [6], anatase/brookite [7]. In this work, we applied three different methods for particle size estimation of TiO₂ polyphasic powder: the direct crystallographic measurement, the use of the Scherrer formula, the use of combination of the Scherrer formula and the Debye equation.

Particle size remains among the most important parameters of substance. The majority of researchers use the Scherrer formula [8] to determine this parameter for the sample nanostructured powder. The result of particle size estimation derived from the Scherrer formula is approximate and based on peak broadening. Although there are numerous refinements of the formula, the issue on the limits of its applicability is still unsolved. The theoretical upper limit of applicability of the Scherrer formula was analyzed in detail and was found for up to 600 nm for LaB₆, Si and CeO₂ [9]. In general case, this value is 11.9 % of extinction length [10]. However, the use of the Scherrer formula provides



a more accurate result in case of measurement of a single reflection [11]. The use of the Debye equation [12] for particle size estimation provides a result of higher accuracy. The Debye equation is used for diffraction pattern modelling on the basis of the intensity of X-ray scattering over interatomic distances. The result derived from this equation is rather precise as it deals with diffuse scattering at each diffraction pattern point, not only at Bragg angles. The Debye equation is applicable to amorphous clusters as well. However, using the Debye equation is rather time-consuming.

The main goal of the current study is to describe the method of estimation of particle size and to apply it to calculate TiO_2 particle size and mass content of two phases of TiO_2 . In our case, TiO_2 powder represents a mixture of anatase and brookite. The proposed method lies in the combination of the Debye equation and the Scherrer formula and allows to estimate the particle size and phase ratio more precisely than using these relations separately.

2. Method

TiO_2 powder was synthesized by the sol-gel method on a *one-pot* principle and represented a mixture of brookite and anatase at a certain ratio. X-ray diffraction (XRD) patterns of all composites were obtained using a Shimadzu MAXima-X XRD-7000 automatic diffractometer ($\lambda=1.5406 \text{ \AA}$ for $\text{CuK}\alpha$ radiation) in the angle interval 2θ of $5\text{--}80^\circ$ with step 0.03° and an exposure time of 10 sec. Calculations at each stage of the method were performed with the use of different software facilities: Powder Cell 2.3, Igor Pro, Crystallmaker, and DIANNA [13].

3. Discussion

X-ray diffraction measurements of TiO_2 powder demonstrates the pure titania without any additives. The experimental diffraction pattern is shown on Fig. 1 with peak positions of anatase and brookite. The majority of peaks contain contributions of more than one reflection. The most of peaks can be referred to anatase, but these broad peaks overlap with peaks of brookite. The only one peak of low-intensity at 30° directly indicates the presence of brookite phase, reflection (211).

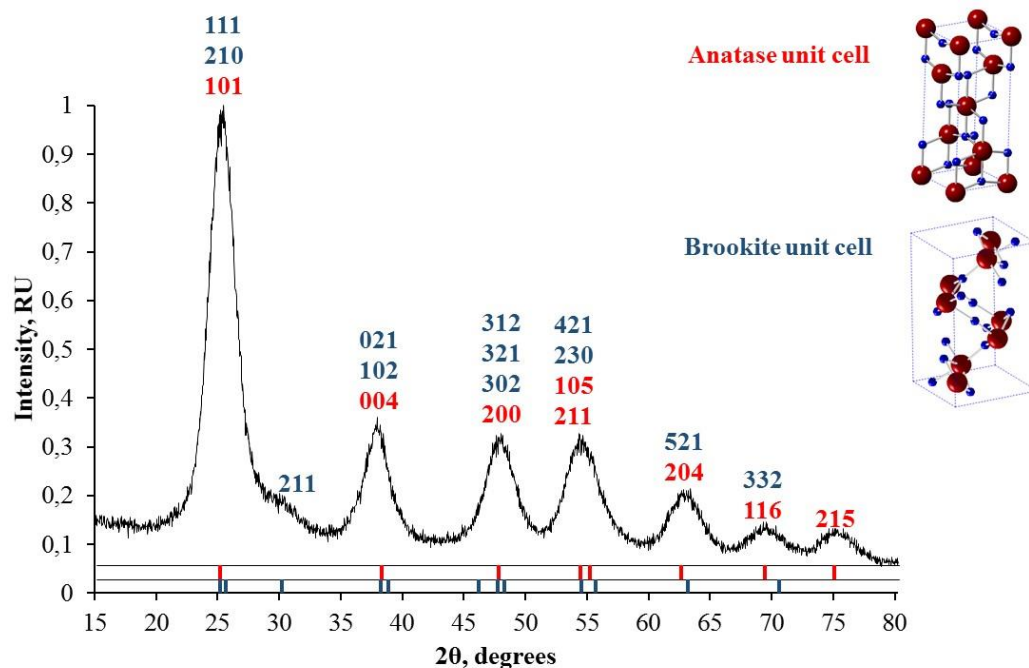


Figure 1. The experimental diffraction pattern of TiO_2 powder. The most intensive reflections of anatase and brookite are shown in the bottom by sticks. The anatase and brookite unit cells are shown in the right part of figure.

Direct calculations of particle size were carried out using software “PowderCell 2.3” and led to ambiguous results. On the Fig. 2a, calculated diffraction peaks (green curve) were obviously narrower than the experimental one (black curve). Moreover, they coincide poorly with the experimental ones in the region $2\theta \approx 30^\circ$. The diameter of anatase particles was determined as 9.1 nm, and the diameter of brookite particles – 8.9 nm. The crystallographic approach could not allow to simulate the very broadening of peaks, and to determine size of very small particles. Thus, the method of particle size estimation based on direct application the Scherrer formula and XRD pattern simulation by the Debye formula is proposed.

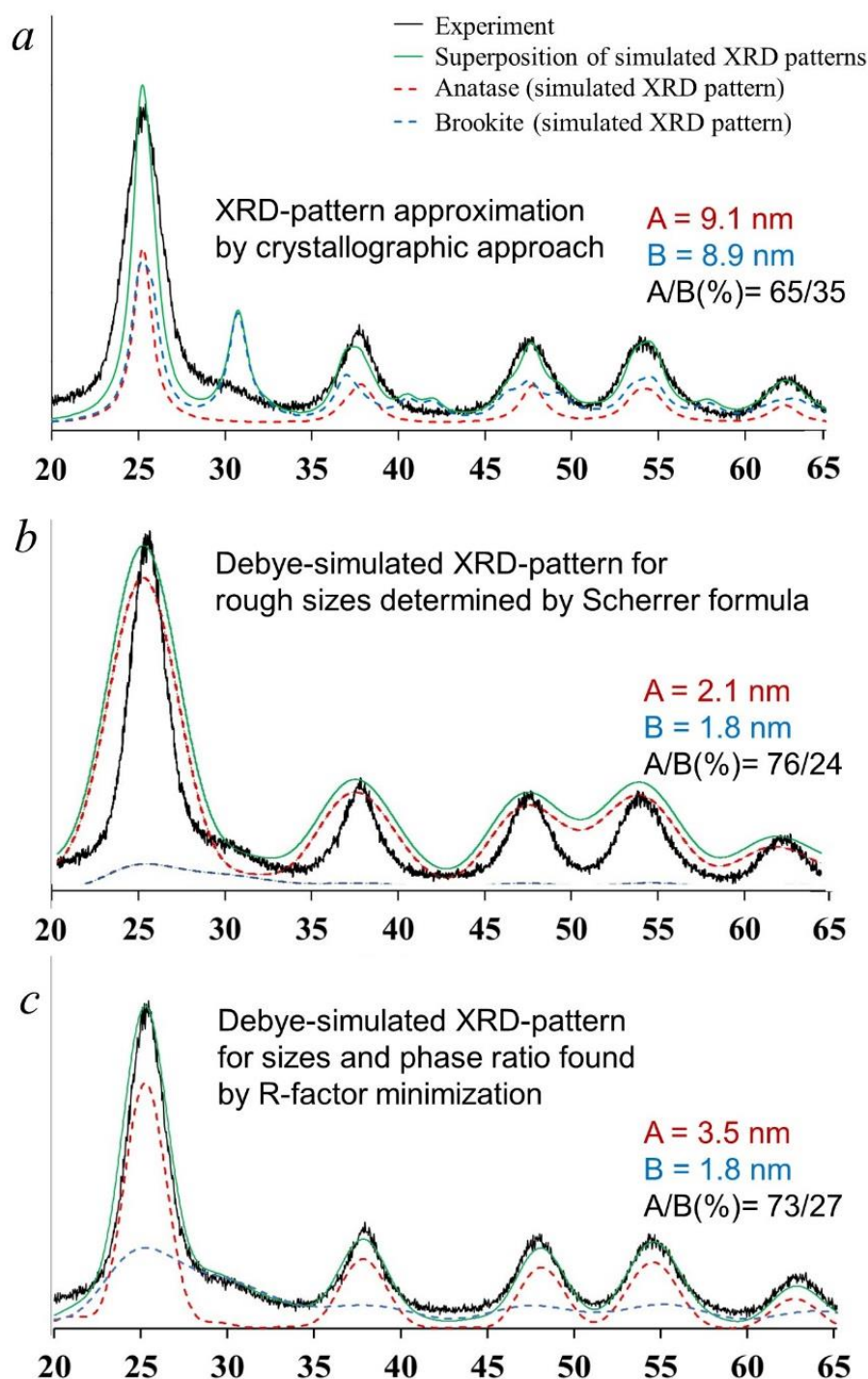


Figure 2. The experimental diffraction pattern (black line) and the theoretical one (green line). The contributions of anatase and brookite are designated by red and blue dash lines correspondingly. The particle size of anatase as A, brookite as B and phase ratio as A/B(%) is shown for each method. The theoretical diffraction pattern was obtained using: (a) by PowderCell 2.3, and by DIANNA for particle size and phase ratio; (b) determined by the Scherrer formula, (c) and determined by R-factor minimization.

The proposed method consists of three steps, which are shown schematically on the Fig. 3.

(i) Calculation of initial value of particle size. The most intensive peak was decomposed into three peaks: anatase reflection (101) and two brookite reflections (210) and (111). Anatase peak (101) and brookite peak (211) were described by Gaussians and calculated the half-width of both reflections. The initial values of the size of anatase and brookite particles were calculated according to the Scherrer formula:

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl} \cos \theta} \quad (1)$$

where K – the particle shape factor, 0.9, λ – X-ray wavelength, β_{hkl} – the half-width of (hkl) reflection, $\theta = 2\theta/2$ – Bragg angle corresponding to (hkl) reflection. The anatase and brookite particle sizes were determined as 2.1 nm and 1.8 nm correspondingly.

Then, we tested the obtained values of particle sizes by simulating of diffraction pattern for these particle diameters using by the Debye equation. We used the software DIANNA [13]. On the Fig. 2b we can see not matching Debye-simulating XRD-pattern and experimental curve. The reason of divergency is the next: the Scherrer formula takes into account broadening of peaks only because of the particle size while in reality, a lot of factors contribute to broadening of peaks. The half-width in the experimental diffraction pattern depends not only on the particle size. It means that the share of the half-width derived from the experimental diffraction pattern, that responsible for broadening of peaks due to the particle size, is actually less than the overall value obtained from direct measurement.

(ii) Refinement of the obtained values. On this step the particle diameter was determined by XRD-pattern simulation using the Debye equation. This approach allowed the direct calculation of XRS-pattern from particle as cluster or, strictly, set of atomic positions. It is possible to calculate the diffraction pattern of any size particles. However, calculation time increases with the particle size. Simulation of the diffraction pattern was carried out with the use DIANNA software [13]. The Debye equation looks as follows:

$$I(s) = P(s) \sum_i \sum_j f_i(s) f_j(s) \frac{\sin(sr_{ij})}{sr_{ij}}, \quad (2)$$

where $s = \frac{4\pi \sin(\theta)}{\lambda}$ is the current reciprocal space coordinate, $P(s)$ – instrumental factor, $f_i(s)$ and $f_j(s)$ are the scattering factors of atoms i and j , respectively.

(iii) Determination of mass content. The sum of simulated pattern from anatase and brookite was compared with experimental pattern by the R-factor. The R-factor reflects the difference between theoretical and experimental diffraction data. The actual ratio corresponds to the minimum R-factor.

Several iterations according to the Debye equation were carried out in order to define more precisely the anatase particles diameter, 3.5 nm. We varied the particle size both anatase and brookite by increment 0.1 nm and compared Debye-simulated XRD-pattern with experimental curve by R-factor. Schematically this procedure is demonstrated on the Fig.3. The result of R-factor minimum searching is demonstrated on the Fig. 2c. The brookite particle diameter remains the same, 1.8 nm. The minimum R-factor corresponds to 27% brookite mass content.

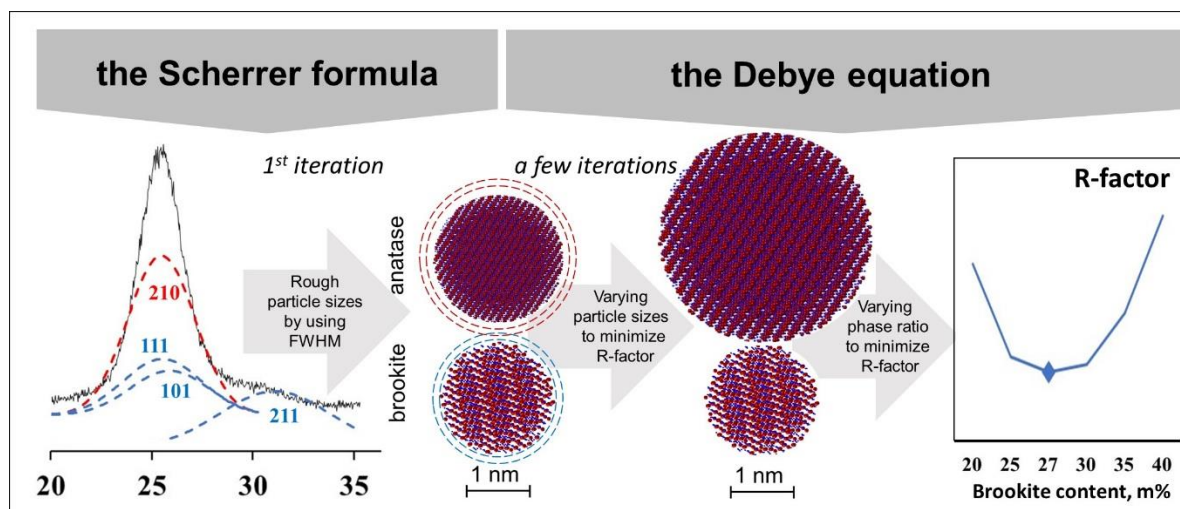


Figure 3. The main steps comprising the proposed algorithm: (i) The decomposition of peaks and calculation of rough values of particle size by using the Scherrer formula and then simulation XRD-pattern for obtained sizes; (ii) Several iterations of the size values variation using by the Debye equation; (iii) the searching of the R-factor minimum for three parameters: two particle sizes and phase ratio. The rough and final results of anatase and brookite particle sizes are shown in scaling. The dependence R-factor from brookite content is shown.

4. Conclusion

In this study, we proposed method which allows to obtain three parameters: diameters of brookite and anatase particles and mass content for TiO_2 polyphasic nanopowder. In the first, we found that the crystallographic approach led to ambiguous results. The anatase and brookite particle sizes are determined 9.1 nm and 8.9 nm correspondingly. Afterwards we calculated directly values of particle size from peak broadening using by the Scherrer formula and found them 2.1 nm for anatase and 1.8 nm for brookite. The nominal obtained values differs more than four times but the values ratio between anatase and brookite both the crystallographic measurement and the Scherrer formula are close to 1. This result pointed the necessity of another approach based on direct simulation of Debye formula. The application of the Scherrer equation and the Debye formula together provided more accurate data, Fig. 2c.

The result obtained by the proposed method was the following: 1.8 nm diameter of brookite particles, 3.5 nm diameter of anatase particles, mass content was 73% of anatase and 27% of brookite phase. The proposed method based on the combination of the Scherrer equation and the Debye formula can be applied to any XRD measurements of nanostructured materials as well.

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